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In this paper we present numerical solution of the linearized and exponential hypervertex approximations for the restricted primitive model for electrolytes. The method of solution is based on a Newton–Raphson scheme previously applied to simple fluids. Thermodynamic results computed from both approximations agree remarkably well with previously published Monte Carlo data even to a greater extent than well-known approximations such as the hypernetted-chain equation.

I. INTRODUCTION

The restricted primitive model (RPM) (equal-sized hard spheres with embedded point charges) is often used to represent ionic solutions (electrolytes) and molten salts. Despite its simplicity it yields excellent results when compared with experimental data for simple electrolytes (such as KCl).[1] Therefore it is of great interest to explore new approximations that can furnish accurate theoretical predictions for its thermodynamic properties. We have considered two approximations which were proposed some time ago by Høye and Stell[2] in the context of the γ ordering in fluids, namely the LHA (linear hypervertex approximation) and EHA (exponential hypervertex approximation). An advantage with respect to the well-known hypernetted-chain equation (HNC) lies in the fact that the RPM reduces to a one-component problem due the linearity in their closure relation, as will be seen in the next section. In this paper we show that both approximations yield results comparable or even superior (in the case of the EHA) to those of the HNC.

II. SUMMARY OF THE THEORY

Here, we will briefly summarize some results in the theory of the LHA and EHA, which can be found in more detail in Ref. 2. The theory as outlined below is restricted to the $Z{:}Z$ RPM (here we have explicitly considered 1:1 and 2:2 electrolytes), although it can be easily extended to any mixture of equal-sized charged hard spheres with arbitrary charges.

One can define the following linear combinations for the total correlation functions between particles of type i and j, $h_{ij}(r)$:

$$h_s(r) = \tfrac{1}{2}[h_{++}(r) + h_{+-}(r)],$$
$$h_d(r) = \tfrac{1}{2}[h_{++}(r) - h_{+-}(r)], \tag{1}$$

and similarly for the direct correlation functions $c_{ij}(r)$. Using the relations $h_{++} = h_{--}$, $h_{+-} = h_{-+}$, and Eq. (1), the Orstein–Zernike (OZ) relation for the RPM reduces to

$$\gamma_s(r_{12}) = \rho \int c_s(r_{13})[\gamma_s(r_{32}) + c_s(r_{32})]d\mathbf{r}_3,$$
$$\gamma_d(r_{12}) = \rho \int c_d(r_{13})[\gamma_d(r_{32}) + c_d(r_{32})]d\mathbf{r}_3, \tag{2}$$

where $\rho = \rho_+ + \rho_-$ (ρ_+ and ρ_- are the cation and anion number densities, respectively) and we have introduced $\gamma = h - c$ for convenience by numerical work. The LHA and EHA closure relations can be written as

$$c_d(r) = -\gamma_d(r) \quad \text{if } r < \sigma,$$
$$c_d(r) = c_d^{\mathrm{SR}} - \beta\phi(r) \quad \text{if } r > \sigma, \tag{3}$$

together with $c_s(r) = c_0(r)$, where this latter function is the direct correlation function for the reference system (uncharged hard spheres). In Eq. (3), $\phi(r) = Z^2e^2/\epsilon r$ is the Coulomb interaction, with Ze as the ion charge and ϵ the dielectric constant of the solvent. Besides, $\beta = 1/kT$, and σ is the hard-sphere diameter. For convenience we define the reduced quantity $\beta^* = \beta e^2/\epsilon\sigma$ which plays the role of an inverse temperature. Next, for h_s one gets

$$h_s(r) = h_0(r). \tag{4}$$

This equation is exact in the LHA theory and is a good approximation in the EHA approach simplifying considerably the computational work. In these approximations corrections to $h_s(r)$ or $c_s(r)$ beyond the reference system are lacking as they are considered to be of higher order. However, such corrections to $c_s(r)$ are present in the HNC and other approximations considered by Stell, Patey, and Høye in their review article.[3] For example, Eq. (2.135b) of Ref. 4 yields explicitly such a correction.

We have computed $h_0(r)$ using the Verlet–Weis parametrization.[5] However, this is not crucial as it has little influence upon thermodynamic quantities. The short-range direct correlation function[2] $c_d^{\mathrm{SR}}(r)$ can be expressed in Fourier space in terms or the hypervertex W_d, which is the short-range part of $h_d(r)$.

$$\tilde{W}_d(k) - \tilde{c}_d^{\mathrm{SR}}(k) = \rho \frac{\tilde{W}_d(k)^2}{1 + \rho\tilde{W}_d(k)}. \tag{5}$$

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Use of the difference $W_d - c_d^{SR}$ is advisable to cope with the hard-core discontinuities present in the functions W_d and c_d^{SR} but absent in their difference.

The approximation of the theory now lies in the hypervertex W_d which can in turn be expressed in terms of the chain bond function L_d and the reference system h_0. In the LHA it is approximated by

$$W_d(r) = h_0(r)L_d(r), \tag{6}$$

and in the EHA

$$W_d(r) = [h_0(r) + 1] \sinh L_d(r) - L_d(r). \tag{7}$$

Finally, the chain bond L_d can be expressed in k space in terms of the perturbing potential function[2]

$$v(r) = c_d(r) - c_d^{SR}(r) \tag{8}$$

[where from Eq. (3) $v(r) = -\beta\phi(r)$ if $r > \sigma$] to give

$$\tilde{L}_d(k) - \tilde{v}(k) = \frac{\rho[1 + \rho\tilde{W}_d(k)]\tilde{v}(k)^2}{1 - \rho[1 + \rho\tilde{W}_d(k)]\tilde{v}(k)}. \tag{9}$$

The iteration procedure can then be summarized as follows.

(1) Given initial estimates of $L_d(r)$ and $\gamma_d(r)$ [notice that $L_d(r) = h_d(r)$ in the mean spherical approximation (MSA)], obtain $W_d(r)$ from the LHA or EHA relations (6) or (7), respectively. Then Fourier transform $W_d(r)$ to compute the difference $\tilde{W}_d(k) - \tilde{c}_d^{SR}(k)$ from Eq. (5), which inverted and combined with $W_d(r)$ renders $c_d^{SR}(r)$.

(2) Use $c_d^{SR}(r)$ in the closure relation (3) to compute a new estimate for $\gamma_d(r)$ solving the OZ equation (2) combined with Eq. (3). The OZ equation in k space reads

$$\tilde{\gamma}_d(k) = \frac{\rho\tilde{c}_d(k)^2}{1 - \rho\tilde{c}_d(k)}. \tag{10}$$

(3) Use the new values of $c_d(r)$ to compute $v(r)$ inside the core from Eq. (8). Then Fourier transform $v(r)$ and use Eq. (9) to generate a new estimate for the chain bond $L_d(r)$. Finally, return to step (1) until convergence is achieved both in $\gamma_d(r)$ and $L_d(r)$.

One may implement efficiently this scheme using a Newton–Raphson–like algorithm analogous to the one proposed by Labik, Malijevsky, and Vonka[7] and further developed by Lomba[6] (see the references for details). Unfortunately, this implementation requires the knowledge of the derivative $\partial\gamma_d(r_i)/\partial c_d(r_j)$ which is not easily computable for the LHA or EHA approximations. Therefore we have used the MSA-like result

$$\frac{\partial\gamma_d(r_i)}{\partial c_d(r_j)} = \begin{cases} -1 & \text{if } |r_i - r_j| < \sigma, \\ 0 & \text{if } |r_i - r_j| \geq \sigma. \end{cases} \tag{11}$$

This gives an approximate Jacobian for the Newton–Raphson procedure which works reasonably well for the systems considered here.

III. RESULTS

We have carried out two sets of calculations in conditions of ionic strength that correspond to 1:1 and 2:2 electrolytes at room temperature. Monte Carlo data were taken from Hansen and McDonald[8] and the classical works by Card and Valleau[9] and Larsen.[4] For completeness we have included several calculations corresponding to the RPM at moderate densities (highly concentrated electrolytes). For the 2:2 electrolyte we have restricted our comparisons with MC data to excess internal energies which are available in the literature.[4]

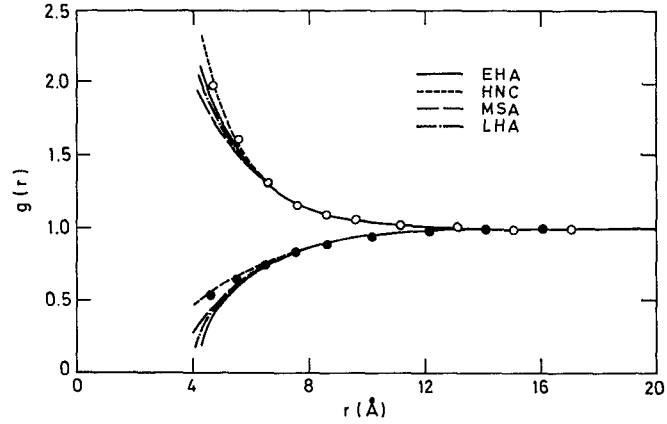

FIG. 1. Ion–ion pair distribution functions for the 1:1 electrolyte ($\beta^* = 1.681$ and $\rho\sigma^3 = 0.0393$): theories vs computer simulation.

Explicit values for the concentrations in the Tables I–V can be recomputed from the reduced densities by using $\sigma = 4.25$ Å, $T = 298.15$ K, and $\epsilon = 78.5$.

A. Radial distribution functions

In Fig. 1 are shown the $g_{+-}(r)$ and $g_{++}(r)$ functions for the 1:1 electrolyte, computed in different approximations and compared with MC data from the work by Card and Valleau.[9] Physical conditions are $\beta^* = 1.681$ and $\rho\sigma^3 = 0.0393$ (which corresponds to $c = 0.425M$ in Ref. 9). As could be expected the LHA and EHA distribution functions give poor agreement with MC results close to the molecular core, as is the case in the MSA. This we attribute to the missing corrections to $h_s(r)$ in our approximations as discussed shortly below Eq. (4).

Consequently, the nonlinear HNC approximation is clearly superior to both hypervertex approximations considered here as far as the structural properties are concerned. However, we will see that the observed deviations in $g_{+-}(r)$ and $g_{++}(r)$ cancel when these quantities are integrated to obtain the thermodynamics.

B. Thermodynamic properties

In Tables I, II, and III we present the results obtained for the excess internal energy $\beta U/N$, Helmholtz free energy $\beta A/N$, and compressibility factor $\beta P/\rho$ (the latter computed via the virial equation), in the LHA and EHA approximations compared with the MSA and HNC results and MC data for the 1:1 electrolyte up to fairly high concentrations.

One can readily observe in Tables I and II that the LHA and especially the EHA yield fairly accurate results in the electrolyte regime. We have found appreciable deviations at high densities (molten salt regime), what may partly be understood as a consequence of the linearity of the closure relation, which does not take properly into account the coupling of electrostatic forces and packing effects. The discrepancy

TABLE I. Excess internal energy $\beta U/N$ for the 1:1 electrolyte: theories vs MC simulation.

$\rho\sigma^3$	c (mol/l)	β^*	MC[a]	LHA	EHA	MSA	HNC
0.0096	0.104	1.681	-0.274 ± 0.001	-0.268	-0.273	-0.267	-0.273
0.0393	0.425	1.681	-0.434 ± 0.002	-0.430	-0.435	-0.426	-0.432
0.0925	1.000	1.681	-0.552 ± 0.002	-0.549	-0.553	-0.540	-0.548
0.1819	1.968	1.681	-0.651 ± 0.002	-0.653	-0.655	-0.636	-0.651
0.2861	3.093	1.882	-0.839 ± 0.030	-0.828	-0.831	-0.804	-0.831
0.2861	3.093	9.411	-5.465 ± 0.080	-5.386	-5.453	-5.278	-5.416

[a] Data taken from Ref. 8.

TABLE II. Excess free energy $\beta A/N$ for the 1:1 electrolyte: theories vs MC simulation.

$\rho\sigma^3$	c (mol/l)	β^*	MC[a]	LHA	EHA	MSA	HNC
0.0096	0.104	1.681	-0.173 ± 0.002	-0.172	-0.171	-0.172	-0.173
0.0393	0.425	1.681	...	-0.235	-0.238	-0.236	-0.238
0.0925	1.000	1.681	...	-0.223	-0.221	-0.212	-0.217
0.1819	1.968	1.681	-0.095 ± 0.010	-0.085	-0.088	-0.072	-0.080
0.2861	3.093	1.882	...	0.076	0.076	0.086	0.076
0.2861	3.093	9.411	...	-3.867	-3.835	-3.770	-3.884

[a] Data taken from Sloth and Sørensen (Ref. 1).

TABLE III. Compressibility factor $\beta P/\rho$ (from the virial equation) for the 1:1 electrolyte: theories vs MC simulation.

$\rho\sigma^3$	c (mol/l)	β^*	MC[a]	LHA	EHA	MSA	HNC
0.0096	0.104	1.681	0.944 ± 0.001	0.931	0.929	0.931	0.945
0.0393	0.425	1.681	0.977 ± 0.005	0.944	0.942	0.945	0.979
0.0925	1.000	1.681	1.094 ± 0.005	1.037	1.036	1.039	1.093
0.1819	1.968	1.681	1.346 ± 0.009	1.275	1.274	1.276	1.353
0.2861	3.093	1.882	0.790 ± 0.310	0.108	0.085	0.130	1.047
0.2861	3.093	9.411	1.620 ± 0.150	1.320	1.627	1.620	1.760

[a] Data taken from Ref. 8.

TABLE IV. Excess internal energy $\beta U/N$ for the 2:2 electrolyte: theories vs MC simulation.

$\rho\sigma^3$	c (mol/l)	β^*	MC[a]	LHA	EHA	MSA	HNC
0.0056	0.063	6.817	-1.893 ± 0.017	-1.456	-1.728	-1.455	-1.737
0.0223	0.250	6.817	-2.473 ± 0.019	-2.184	-2.371	-2.178	-2.365
0.0502	0.563	6.817	-2.822 ± 0.008	-2.660	-2.792	-2.643	-2.757
0.0892	1.000	6.817	-3.091 ± 0.011	-3.011	-3.101	-2.979	-3.041
0.1785	2.000	6.817	-3.509 ± 0.016	-3.432	-3.490	-3.380	-3.396

[a] Data taken from Ref. 4

in $\beta P/\rho$ may also partly be affected by the obvious correction to $h_s(r)$, as noted above.

As for the 2:2 electrolyte, the main results are contained in Tables IV and V. In Table IV we compare our internal energy results with MC data, and MSA and HNC values. Again we observe that the EHA matches the HNC approximation at very low densities and it is slightly more accurate at higher densities. The LHA in the dilute regime hardly differs from the MSA results but improves considerably at higher concentrations. Finally, in Table V we summarize the results obtained for other thermodynamic properties.

IV. CONCLUDING REMARKS

We have shown that both the LHA and EHA yield results for the thermodynamic properties for the RPM in close agreement with MC simulation and comparable to those of approximations of the HNC, whereas retaining the simplifying reduction of the RPM to a one-component problem. We consider this as a good starting point to extend these sort of theories to cope with the ion-pairing problem or chemical association in the context of the γ ordering.[10] In this way, one may try to bring the theoretical results to closer agree-

TABLE V. Excess free energy $\beta A/N$ and compressibility factor $\beta P/\rho$ for the 2:2 electrolyte in the EHA and LHA approximations.

			$\beta P/\rho$		$\beta A/N$	
$\rho\sigma^3$	c (mol/l)	β^*	LHA	EHA	LHA	EHA
0.0056	0.063	6.817	0.526	0.436	−1.071	−1.369
0.0223	0.250	6.817	0.320	0.258	−1.603	−1.613
0.0502	0.563	6.817	0.226	0.182	−1.909	−1.876
0.0892	1.000	6.817	0.207	0.177	−2.069	−2.087
0.1785	2.000	6.817	0.335	0.315	−2.151	−2.130

ment with the exact lower bounds for the vapor pressure reported by Gillan.[11] For the two-dimensional electrolyte or Coulomb gas the effect of chemical association has already been considered more explicitly by Høye and Olaussen in this respect.[12] By their analysis they obtained results that support the asymptotic qualitative features obtained earlier by Kosterlitz and Thouless in a different context by an analysis restricted to the logarithmic Coulomb interaction.[13] The most characteristic feature of this latter system is the Kosterlitz–Thouless phase transition beyond which there will be no free ions to give Debye shielding as they all will be bound into neutral pairs (molecules).

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